Development of $LiNi_{0.5}Mn_{1.5-x}Ti_xO_4$ as an Advanced Cathode for Lithium-Ion Batteries

Uudergraduate Honors Thesis

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4/13/2018

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Abstract

After their successful application in small electronics, lithium-ion (Li-ion) batteries have been developed in ever larger sizes to support the energy and power requirements needed for electric vehicles (EVs). To further extend the driving distance of EVs at lower cost, there has been extensive research efforts in developing next-generation battery materials with higher energy density. $LiNi_{0.5}Mn_{1.5}O_4$ (LNMO) is a promising cathode material due to its high operating voltage of 4.7 V. However, LNMO has short cycle life issue attributed to its unwanted surficial reactions in contact with liquid electrolytes. As a solution, partial Ti substituting for Mn in LNMO was demonstrated to stabilize the particle surfaces and consequently improve the cycle life. The amount of Ti substation, however, is limited because of unexpected capacity decrease with increasing Ti content, x, in $LiNi_{0.5}Mn_{1.5-x}Ti_xO_4$. We hypothesized that such a capacity reduction is caused by a decrease in electrical conductivity; Ti^{4+} has no electron at its d-orbital, and increasing Ti content in $LiNi_{0.5}Mn_{1.5-x}Ti_xO_4$ reduces the charge carrier concentration. Though the research, my objective is to examine this hypothesis by experiments, and propose a strategy to improve the specific capacity of the $LiNi_{0.5}Mn_{1.5-x}Ti_xO_4$. I first synthesized $LiNi_{0.5}Mn_{1.0}Ti_{0.5}O_4$ by a sol-gel method. I reduced the particle sizes of the resulting powder, and applied carbon coating that in theory can improve the electrical conductivity between particles. I processed the resulting powders as a cathode for coin-type Li-ion battery cells, and assessed their electrochemical performance by using Arbin battery testing system. I will discuss about the effect of particle

modification (e.g., size, conductive coating) on the electrochemical properties of $LiNi_{0.5}Mn_{1.0}Ti_{0.5}O_4$ as a cathode in Li-ion battery cells.

Acknowledgement

First, I want to give my special thanks to my advisor, Dr. Jung-Hyun Kim, who give me the opportunity to participate in this research. He was always willing to give me guidance throughout the research, discussing the barriers encountered in the research. Under his supervision, I not only learn more knowledge on batteries but also learned the spirit and methodology of conducting research.

I also want thank Dr. Anne Co and Daniel Lyons for allowing me to use the tubular furnace in their lab. Carbon coating is a crucial step in the research and I could not finish my project in time without their assistance.

I owe a huge thank to Chanyeop Yu, who give me help throughout this research. I would never finish my research without him. He is a very patient and circumspective person with a great understanding of Lithium ion Battery. He taught me how to use all types of machines, the detailed of every experiment procedure; he also helped me conduct the XRD and SEM examination while I do not have the access. I also want to thank Cody O'Meara, he taught me basic knowledge of batteries and answered many doubts I have in the lab.

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Chapter 1: Introduction

1.1 Introduction of Lithium-ion Battery

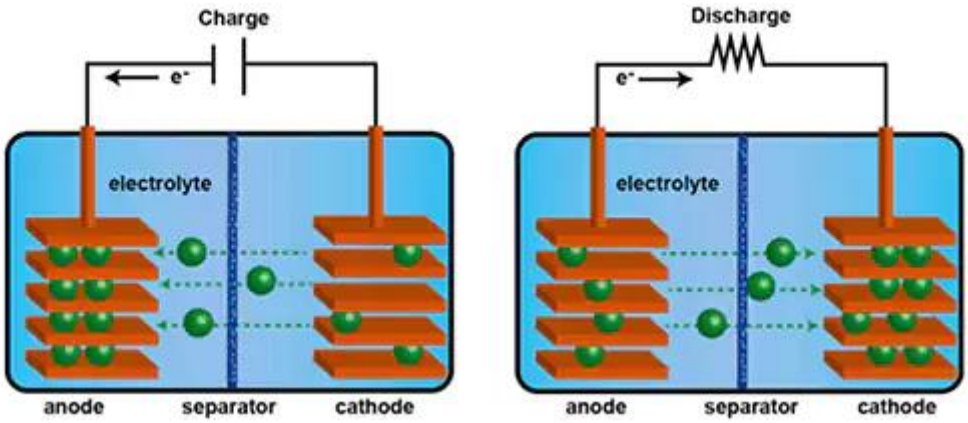

Figure 1: Lithium battery diagram

Lithium-ion battery is one of the most common used rechargeable battery in people's daily life. It has a variety of application from cellphones, laptops to large machines and vehicles. The reason for wide range of use of Lithium ion battery is because its high energy density which means that it can provide more power than other types of rechargeable battery with a smaller space and less weight while safe to operate. There are main four components for lithium-ion battery shown in Figure 1[1], cathode, anode, separator and electrolyte. During the charging cycle, lithium ion moves from cathode to anode and during discharging cycle, lithium ion would move from anode to cathode to provide a current to the load. The focus of this research would be on the improvement of the cathode material.

$LiNi_{0.5}Mn_{1.5}O_4$ (LNMO) is a promising candidate as the positive electrode for its high operating voltage ~4.7 V and high energy density. In addition, low cost and low toxicity are

also advantages for LNMO. Although LNMO delivers good battery performance, there is a significant problem of poor life cycle reported by recent studies. Having such high operating voltage would provide a strongly oxidizing environment resulting in electrolyte decomposition. The oxidative decomposition of electrolyte would occur at the interface of the cathode and the electrolyte and generates various reaction byproducts such as HF, Mn^{2+} and Ni^{2+}. These byproducts destabilize the solid/electrolyte interface (SEI) layer on the anode, which leads to continuous growth of the SEI with additional Li^{+} consumption. By losing active Li^{+}, the battery lose capacity and will eventually fail.

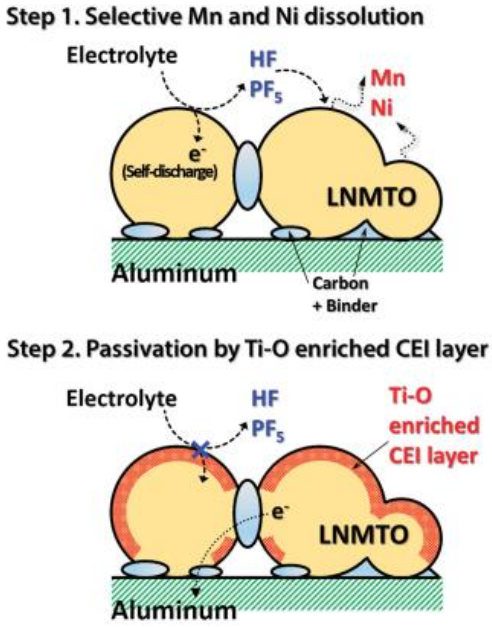

Figure 2:Illustration of the formation mechanism of the CEI on LNMTO cathode. [2]

One possible approach for improving the cycling life of LNMO is a partial substitution of Mn with Ti, using $LiNi_{0.5}Mn_{1.5-x}Ti_xO_4$ as cathode. Figure 2 demonstrates the improvement mechanism of the $LiNi_{0.5}Mn_{1.5-x}Ti_xO_4$ by forming a Ti-O enriched passivation layer after

sacrificial dissolution of Mn^{2+} and Ni^{2+} from the cathode. [2] The presence of such passivation layer mitigates the corrosion reactions at the surface of cathode particles, and thereby improves the cycle life of Li-ion battery cells. [2]

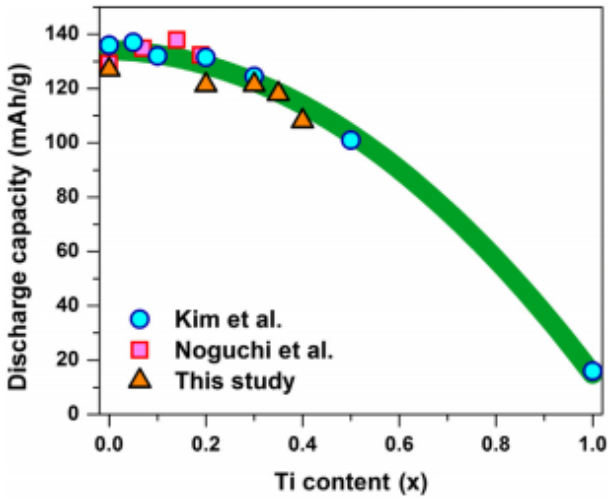

Figure 3：Discharge capacity vs. Ti content

However, $LiNi_{0.5}Mn_{1.5-x}Ti_xO_4$ showed a decrease in specific capacities with increasing Ti contents in Li-ion battery cells, as shown in Figure 3. Since $LiNi_{0.5}Mn_{1.5-x}Ti_xO_4$ deliver capacity via $Ni^{2+/4+}$ redox reactions during charge/discharge of cells, replacing the electrochemically inactive Mn with Ti should not vary the capacity of the material.

1.2 Significance of Research

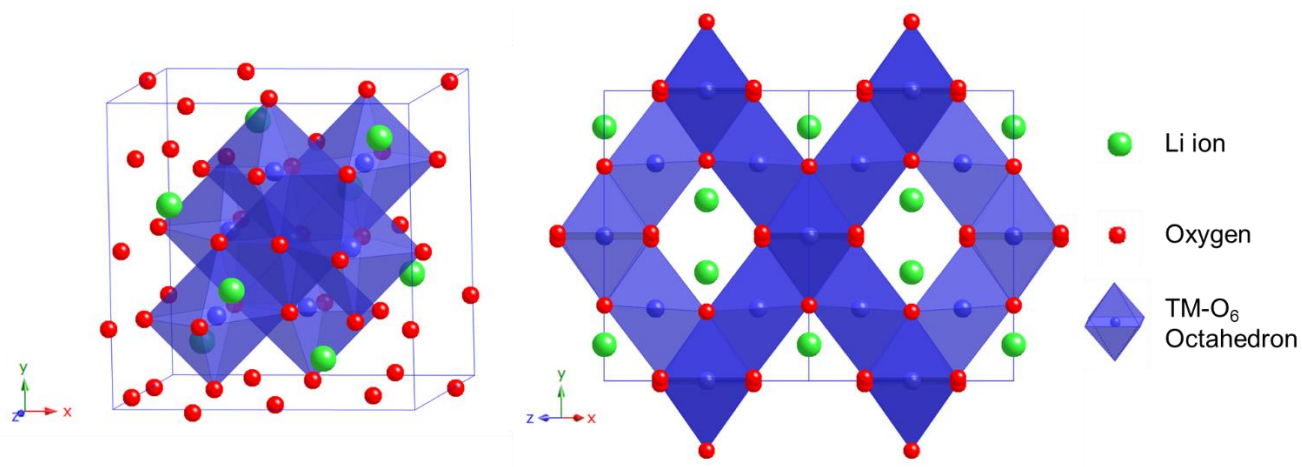

Figure 4: Crystal Structure of LNMO

To explain this behavior, Dr. Kim hypothesized that such a capacity decrease is caused by a decrease in electrical conductivity; Ti^{4+} has no electron at its *d*-orbital, and increasing Ti content in $LiNi_{0.5}Mn_{1.5-x}Ti_xO_4$ reduce the charge carrier (i.e., electron) concentration.[3] Based on this understanding, I plan to examine this hypothesis by experiments, and propose a strategy to improve the specific capacity of the $LiNi_{0.5}Mn_{1.5-x}Ti_xO_4$, which is an important step for its Li-ion battery applications.

1.3 Overview of Thesis

In chapter 2, the experiment procedure will be explained. Chapter 2.1 will introduce the synthesize process of the cathode material. 2.1.1 will discuss the synthesize of LNMO and 2.1.2 will discuss the synthesize of LNMTO. Chapter 2.2 will illustrate the carbon coating process for LNMO and LNMTO, 2.2.1 will talk about the carbon coating proceed in argon atmosphere and 2.2.2 while discuss the carbon coating process in air atmosphere.

Chapter 2.3 mainly discuss transforming cathode material to actual testing. In 2.3.1, I will discuss the procedure of making cathode and I will talk about the process of making coin cell battery in 2.3.2. In 2.3.3, I will explain the procedure of testing the fabricated coin cell. In chapter 3, I will discuss the result of X-ray diffraction result, Scanning electron microscopy result and coin cell test data and I will sum up about the research contribution to the industry and future work in given more time in chapter 4.

Chapter 2 Experiment Procedure

2.1 Material Synthesis

2.1.1 Synthesize $LiNi_{0.5}Mn_{1.5}O_4$ (LNMO) Cathode Material

The original method to synthesize $LiNi_{0.5}Mn_{1.5}O_4$ was to conduct solid-state reaction method. However, due to the limitation of equipment and considering the solid-state method would create the material in a relatively large particle size, sol-gel method was decided to be the method of synthesizing $LiNi_{0.5}Mn_{1.5}O_4$. LiCl, $NiCl_2 \cdot 6H_2O$, $MnCl_2 \cdot 4H2O$ are selected as the materials to synthesize $LiNi_{0.5}Mn_{1.5}O_4$. I decided to first make 3 grams of LNMO and the stoichiometric amount of each material is determined using following train of thought. I first looked up the atomic weight of each element and determined their stoichiometric amount to calculate the total atomic weight of LNMO using the table 1 below.

Table 1: $LiNi_{0.5}Mn_{1.5}O_4$ weight for each element

Elements	Atomic weight	Stoichiometry	
Li	6.941	1	6.941
Ni	58.693	0.5	29.3465
Mn	54.938	1.5	82.407
O	15.999	4	63.996
Ti	47.88		0
		LNMO Atomic weight	182.6905

After calculating the atomic weight of each element, the moles of LNMO needed is determined using the following equation:

$$\text{Moles of LNMO} = \frac{Weight\ of\ LNMO}{Atomic\ weight\ of\ LNMO} = \frac{3g}{182.6905g/mol} = 0.016mole$$

For the convenience of calculation, 0.015 moles of LNMO has decided to be synthesize. To determine the amount of chemicals to synthesize LNMO, I listed the

molecular weight of each chemicals in the table 2 below. Additional 5% of LiCl is added considering that Lithium would evaporate during the further heat treatment. The total mass of each material is calculated using the following equation.

Table 2: Molecular weight of chemicals (LNMO)

Chemical	Molecular Weight (g/mol)	Stoichiometry	Moles	Total mass (g)
LiCl	42.394	1	0.015	0.6677055
NiCl2, 6H2O	237.71	0.5	0.015	1.782825
MnCl2, 4H2O	197.9	1.5	0.015	4.45275

$$\text{Total mass of each chemical} = \text{Molecular weight} \times \text{Stoichimotery} \times \text{mole}$$

After determining the mass for each chemical, 50 ml of de-ionized water is measured using volumetric cylinder and pour into the beaker. The determined amount of chemicals is weighted using balance. All chemicals were dissolved in the de-ionized water, and the beaker was placed on the hot plate. Oxalic acid was added as the cleating agent and the solution was dried to gel state under continuous stirring and heating. (130℃ 260 rpm).

Figure 5: Dried gel state of $LiNi_{0.5}Mn_{1.5}O_4$

The dried gel was transformed into powder state by conducting heat treatment. The gel was placed at the furnace at room temperature and the temperature was raised in a rate of

3℃/min to 400 ℃. $LiNi_{0.5}Mn_{1.5}O_4$ was sintered at 400 ℃ for 3 hours and the temperature raised to 700℃ under the same rate for $LiNi_{0.5}Mn_{1.5}O_4$ was heated for another 10 hours. The temperature dropped to room temperature in the rate of 3℃/min and became to powders.

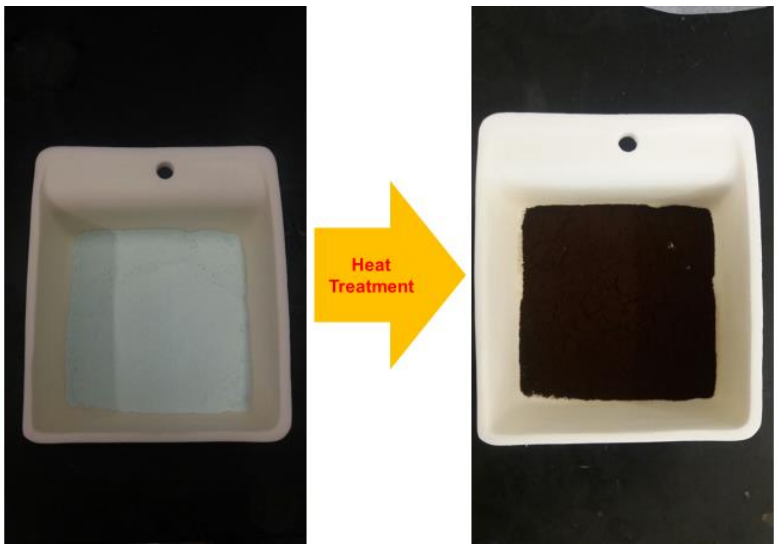

Figure 6: Heat Treatment of $LiNi_{0.5}Mn_{1.5}O_4$

To confirm the components of the synthesized material, an XRD test was conducted.

After confirming the composition of the material, a SEM examination was conducted to observe the particle size of the synthesized material.

To obtain a better crystallinity of $LiNi_{0.5}Mn_{1.5}O_4$, part of the powder was heated in the furnace again for 3 hours under 800 ℃.

2.1.2 Synthesize $LiNi_{0.5}Mn_1Ti_{0.5}O_4$ (LNMTO) Cathode Material

$LiNi_{0.5}Mn_1Ti_{0.5}O_4$ is also synthesized using sol-gel method. LiCl, $NiCl_2 \cdot 6H_2O$, $MnCl_2 \cdot 4H2O$ and Titanium Butoxide was selected as the raw material for the synthesis. I

looked up the atomic weight of each element and determined their stoichiometric amount to calculate the total atomic weight of LNMO using the table 3 below.

Table 3: Weight for each element (LNMTO)

Elements	Atomic weight	Stoichiometry	
Li	6.941	1	6.941
Ni	58.693	0.5	29.3465
Mn	54.938	1	54.938
O	15.999	4	63.996
Ti	47.88	0.5	23.94
		LNMO Atomic weight	179.1615

After calculating the atomic weight of each element, the moles of LNMTO need to be made is determined using the following equation:

$$\text{Moles of LNMTO} = \frac{Weight\ of\ LNMTO}{Atomic\ weight\ of\ LNMTO} = \frac{3g}{179.1615g/mol} = 0.017mole$$

After calculation, 0.015 moles of LNMTO has decided to be made. To determine the amount of chemicals to synthesize LNMTO, I listed the molecular weight of each chemicals in the table below. Additional 5% of LiCl is added considering that Lithium would evaporate during the further heat treatment. The total mass of each material is calculated using the following equation.

Table 4: Molecular weight of chemicals (LNMTO)

Chemical	Molecular Weight (g/mol)	Stoichiometry	Moles	Total mass (g)
LiCl	42.394	1	0.015	0.6677055
NiCl2, 6H2O	237.71	0.5	0.015	1.782825
MnCl2, 4H2O	197.9	1	0.015	2.9685
Ti-butoxide	340.36	0.5	0.015	2.5527

$$\text{Total mass of each chemical} = \text{Molecular weight} \times \text{Stoichimotery} \times \text{mole}$$

The procedure of synthesizing is identical to the procedure of synthesizing LNMO. After finish synthesizing, an XRD test was conducted to confirm the components of the synthesized material.

After confirming the composition of the material, a SEM examination was conducted to observe the particle size of the synthesized material.

Part of the powder LNMT5 was heated in the furnace again for 3 hours under 800 ℃ to obtain better crystallinity.

2.2 Carbon coating for $LiNi_{0.5}Mn_{1.5}O_4$ and $LiNi_{0.5}Mn_1Ti_{0.5}O_4$

2.2.1 Carbon coating in Argon atmosphere

After successfully synthesized both $LiNi_{0.5}Mn_{.1.5}O_4$ and $LiNi_{0.5}Mn_1Ti_{0.5}O_4$, the next step is to apply carbon coating on the cathode material. PAA is selected to be the material that would provide Carbon element to the cathode material. I determined to apply 30 weight percent of the carbon coating for the cathode material.

I first weight 0.1 g of the material using the balance and a 25-weight percent of the PAA solution is used to apply carbon coating, the weight of PAA solution is calculated using the equation below.

$$\text{Weight of PAA solution} = \text{Weight of the cathode mateiral} \times \%\ \text{weightof carbon coating} \times \%\text{weight of PAA solution} = 0.1\text{g} \times 30\% \times 25\% = 0.12\text{g}$$

After weighing, I dissolved the cathode material and PAA solution into 20 ml of de-ionized water and use hot plate to dry out the liquid with high temperature and continues stirring.

When the solution is completely dried, the material is well mixed and sent into Argon tubular furnace. The furnace was initially set at room temperature and the temperature was raised in a rate of 3℃/min to 500 ℃. The carbon coated material was sintered at 500 ℃ for 5 hours and the temperature dropped back to the room temperature under the same rate.

An XRD examination has been conducted to insure the cathode material remain to be LNMO and LNMTO.

2.2.2 Carbon coating in air atmosphere

Same amount of PAA solution has been sufficiently mixed with 0.1 g of LNMO and LNMT5 taking the same procedure of carbon coating in argon atmosphere. After drying the liquid, the furnace was preheated to 500 ℃. I put the carbon coated LNMO and LNMT5 into the furnace and heated for 10 minutes and then took the cathode material out and quench to room temperature.

An XRD examination has been conducted to insure the cathode material remain to be LNMO and LNMTO.

2.3 Coin cell making and testing

2.3.1 Cathode making

After finishing carbon coating for $LiNi_{0.5}Mn_{.1.5}O_4$ and $LiNi_{0.5}Mn_1Ti_{0.5}O_4$, the next step is to make cathodes using the powders. I have a total of 8 cathodes using $LiNi_{0.5}Mn_{.1.5}O_4$ under

700 ℃ and 800 ℃, $LiNi_{0.5}Mn_1Ti_{0.5}O_4$ under 700 ℃ and 800 ℃ and carbon coated $LiNi_{0.5}Mn_{.1.5}O_4$ under 700 ℃ and 800 ℃ and $LiNi_{0.5}Mn_1Ti_{0.5}O_4$ under 700 ℃ and 800 ℃.

The cathode material has 3 components: the active material which is the powders that has been previously synthesized, the conductive agent which is carbon black and the binder, PVDF. The weight distribution is 80% of the active material, 10% of the conductive agent and 10% of the binder. After weighing the stoichiometric amount of each material, I put them in the mortar and carefully mixed until all materials are well spread. (No white powder can be observed). About 0.15 ml of NMP to the mixing powder, and the solution is carefully grind to glue state. An aluminum foil was flatly laid on the glass and the gel state cathode material was attached to the foil using Dr. Blade with a thickness of 0.25mm or 0.15 mm depending on the amount of the material. Figure 5 was showing the gel state cathode material before drying.

Figure 7: gel-state cathode material

The cathode was put in the vacuum oven and was heated at 80 ℃ for 1 hour to evaporate the moisture. After drying the material, the cathode cut to round pieces using parafilm and was stored in the vacuum oven overnight to insure no moisture is in the cathode.

2.3.2 Fabricating Li-ion coin cell

After making cathodes for $LiNi_{0.5}Mn_{.1.5}O_4$ and $LiNi_{0.5}Mn_1Ti_{0.5}O_4$ under 700 ℃ and 800 ℃ and carbon coated $LiNi_{0.5}Mn_{.1.5}O_4$ and $LiNi_{0.5}Mn_1Ti_{0.5}O_4$ under 700 ℃ and 800 ℃, I decided to evaluate the specific capacities of all made cathodes by fabricating a coin-type Li-ion battery cells shown in Figure 6.

Figure 8: Coin-cell Battery

To prevent oxidization for all material, the procedure is completed in a glove box filled with argon gas shown in Figure 7. The first step of making a coin cell battery is to place the top of the battery case in an upside-down direction, then place a ring and two disks on top the case. Li metal is placed on the disk and the separator is on top of the Li metal. A few drops electrolyte on top of the Lithium metal and the cathode is laid on top of the separator (the side with cathode material is attaching to the separator). To make sure the electrolyte is filled in the coin cell battery, another 2 drops of electrolyte is added to the battery. For the last step, the bottom case of the battery is attached to the battery and the coin cell was clamped using clamping machine with a pressure around 1000 psi. The coin cell went through an initial test using voltmeter to determine if it can be used for further testing. If an apparent voltage is displayed on the voltmeter, the coin cell is indicated to be functional.

Figure 9: Glove Box

2.3.3 Coin cell battery testing

After fabricating coin cell batteries for $LiNi_{0.5}Mn_{.1.5}O_4$ and $LiNi_{0.5}Mn_1Ti_{0.5}O_4$ under 700 ℃ and 800 ℃ and carbon coated $LiNi_{0.5}Mn_{.1.5}O_4$ and $LiNi_{0.5}Mn_1Ti_{0.5}O_4$ under 700 ℃ and 800 ℃, the coin cell tested using Arbin battery testing system shown in Figure 8.

Figure 10: Arbin battery testing system

The newly made coin cell batteries will be set for rest 24 hours, then the battery will be charged under 0.1 C-rate (10 hours to fully charged) and rest for 10 minutes and discharged under the same rate. This cycle will be repeated for 50 times to observe the specific capacity the cycle life of each coin cell battery. The capacity of the battery will be recorded for every 10 minutes or every voltage change for 0.05V.

Chapter 3 Result and Discussion

3.1 X-ray Powder Diffraction (XRD)

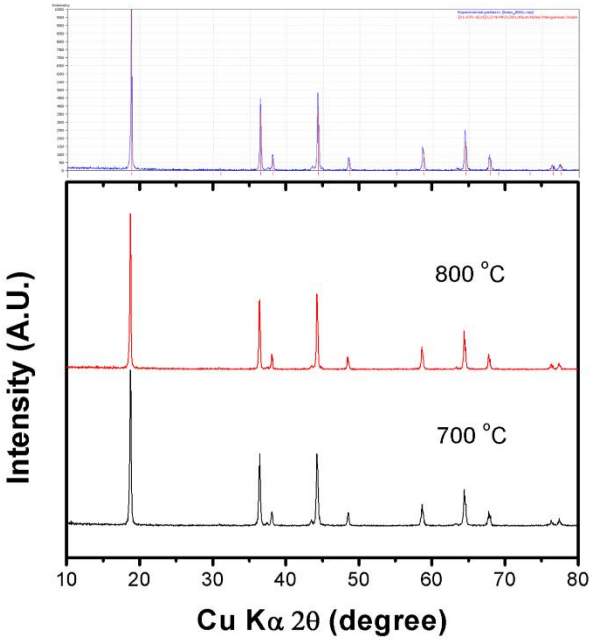

Figure 11: XRD patterns of $LiNi_{0.5}Mn_{1.5}O_4$ sintered at 700℃and 800℃

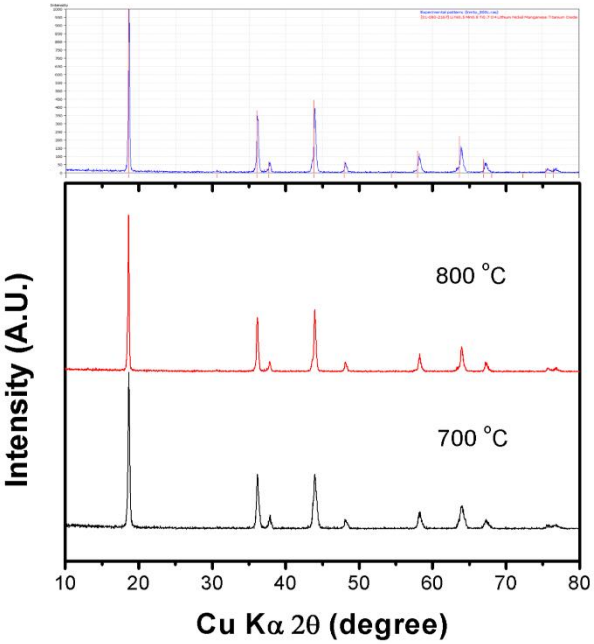

Figure 12: XRD patterns of $LiNi_{0.5}Mn_1Ti_{0.5}O_4$ sintered at 700℃and 800℃

Both $LiNi_{0.5}Mn_{1.5}O_4$ and $LiNi_{0.5}Mn_{1.0}Ti_{0.5}O_4$ were synthesized using sol-gel method and heated at 700℃ and 800℃. As shown in Figure 11 and Figure 12, the XRD patterns has shown a clear single-phase diagram with little noise. On the top of each Figure, reference XRD data are presented. The index of the peaks corresponds with the XRD pattern of previously made LNMO and LNMTO powders which demonstrate that $LiNi_{0.5}Mn_1Ti_{0.5}O_4$ and $LiNi_{0.5}Mn_1Ti_{0.5}O_4$ is successfully synthesized using sol-gel method.

3.2 Scanning Electron Microscopy (SEM) test for LNMO and LNMTO

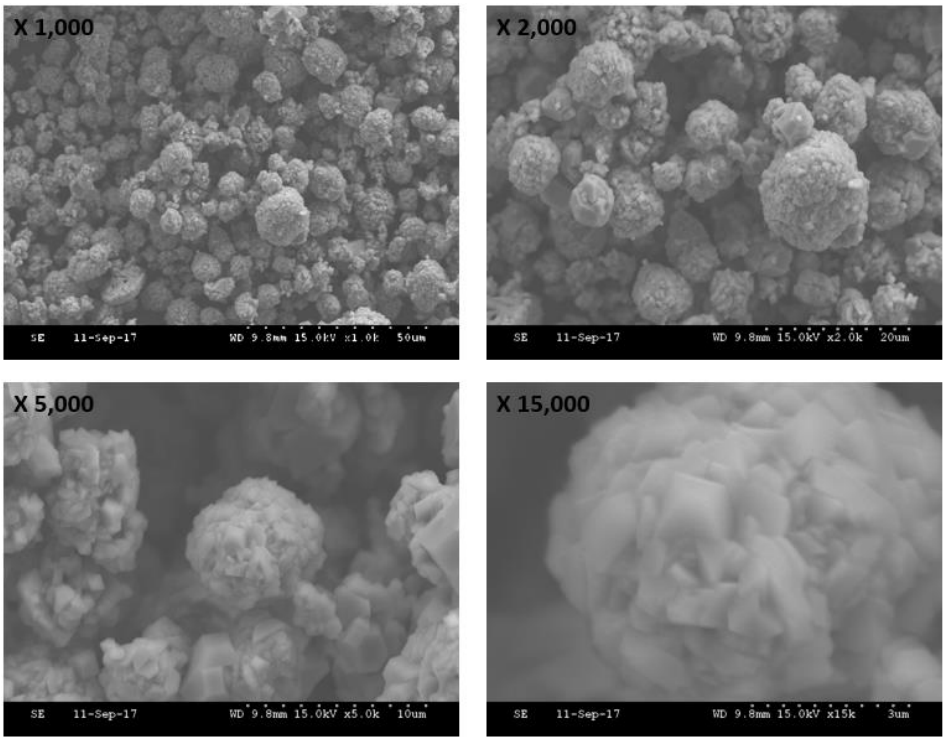

Figure 13: SEM image for Commercial $LiNi_{0.5}Mn_{1.5}O_4$

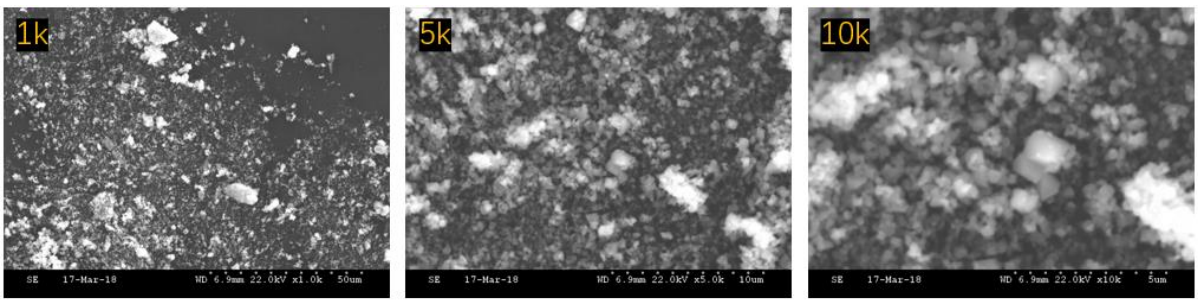

Figure 14: SEM images for $LiNi_{0.5}Mn_{1.5}O_4$ synthesized by sol-gel process

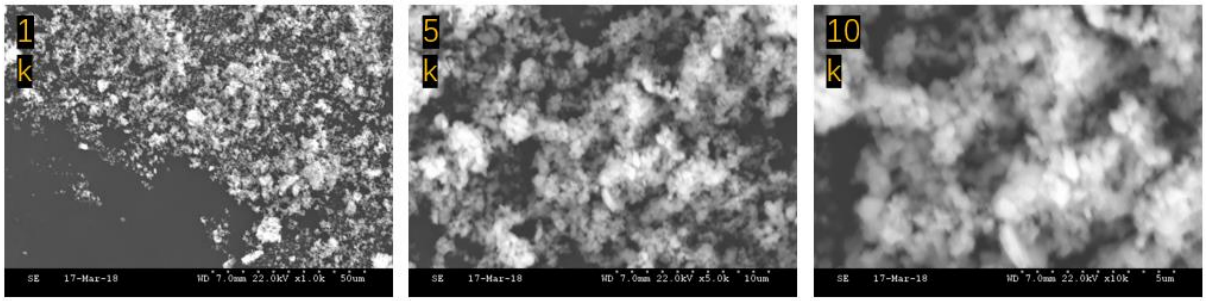

Figure 15: SEM image for $LiNi_{0.5}Mn_1Ti_{0.5}O_4$ synthesized by sol-gel process

An Scanning electron microscopy test (SEM) has been carried out to compare the commercial LNMO and the LNMO and LNMTO synthesized using sol-gel method. According to the SEM images in Figure 13, the LNMO powder purchased from MTI has a primary particle sized for 5~10 μm observed from 15000 magnification, and a secondary particle size around 30~50 μm observed in 2000 and 5000 magnification.

On the other hand, for the $LiNi_{0.5}Mn_{1.5}O_4$ and $LiNi_{0.5}Mn_1Ti_{0.5}O_4$ synthesized using sol-gel method shown in Figure 14 and 15, through the 10000 magnification, it can be observed that the primary particle size is in nano-scale, and the secondary particle size is around 5~10 μm. This indicate that the particle sized has been decreased using sol-gel method combined with grinding.

3.3 Carbon coating in Argon and Air atmosphere

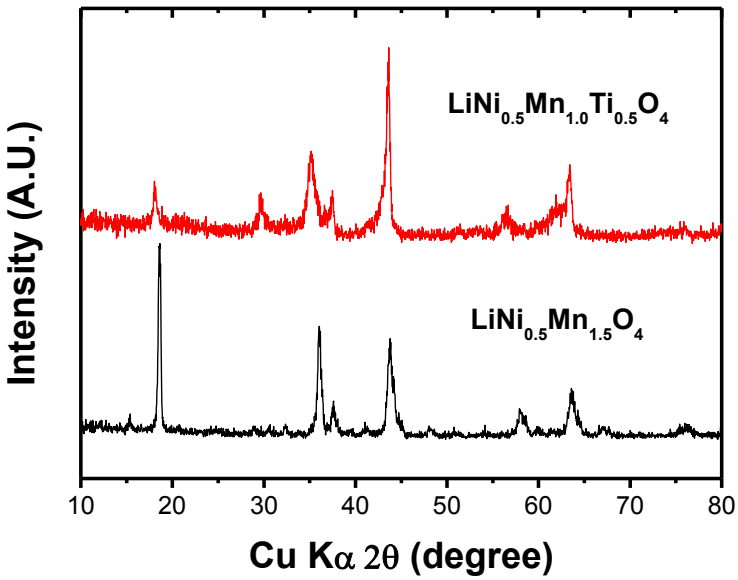

Figure 16: XRD patterns of carbon-coated $LiNi_{0.5}Mn_{1.5}O_4$ (bottom) and $LiNi_{0.5}Mn_1Ti_{0.5}O_4$ heated in Argon

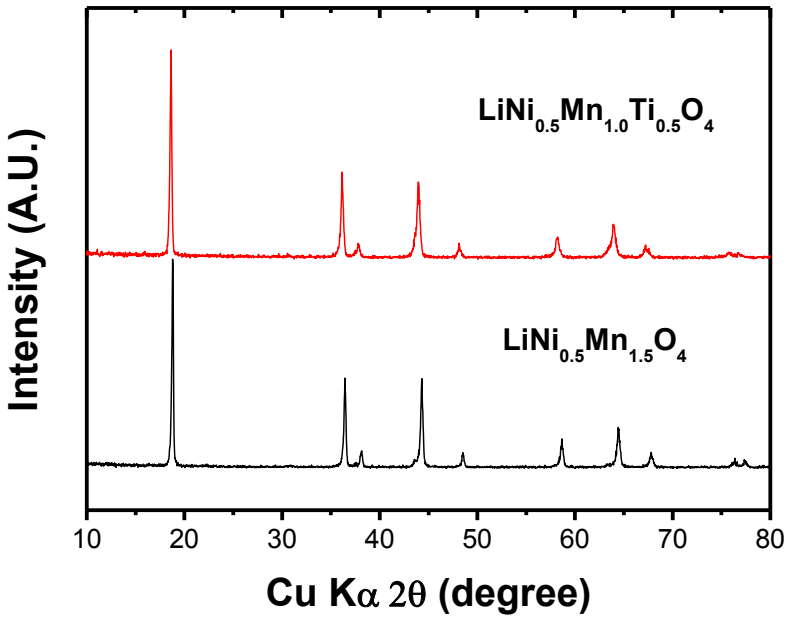

Figure 17: XRD patterns of carbon-coated $LiNi_{0.5}Mn_{1.5}O_4$ (bottom) and $LiNi_{0.5}Mn_1Ti_{i0.5}O_4$ heated in air

According to XRD pattern showed in Figure 16, the synthesized $LiNi_{0.5}Mn_{1.5}O_4$ and $LiNi_{0.5}Mn_1Ti_{0.5}O_4$ is decomposed in the carbon coating process in Argon atmosphere. Noise

can be clearly observed for both material, especially LNMO, and some peaks has shifted for LNMO and also some peaks for LNMTO also does not reached the desired intensity. The potential reason for the decomposition reaction is that carbon might reaction with the oxygen elements in LNMO and LNMTO, causing products like carbon dioxide and lithium oxide to be evaporate.

After knowing this error, carbon coating was reconducted using a different approach. By heating directly in a high temperature (500℃) for 10 minutes in air atmosphere, carbon coating is successfully applied to both materials while maintaining their original composition. This can be demonstrated by Figure 17, as the XRD pattern for both materials are identical to the previous measured XRD pattern.

3.4 Coin cell test result

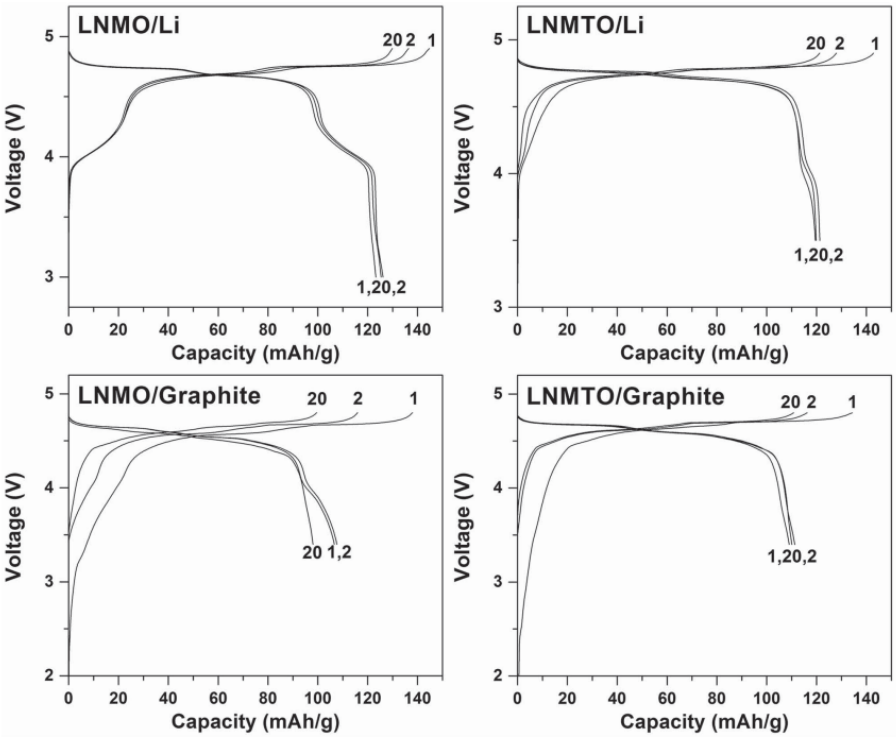

Figure 18: Voltage profiles of LNMO and $LiNi_{0.5}Mn_{1.2}Ti_{0.3}O_4$ (LNMTO) spinel cathodes paired with Li (half cells) or graphite (full cells) anodes. The 1st, 2nd, and 20th cycle data were compared. The cells were cycled in a voltage range of 3.5–4.9 V for half cells and 3.4–4.8 V [2]

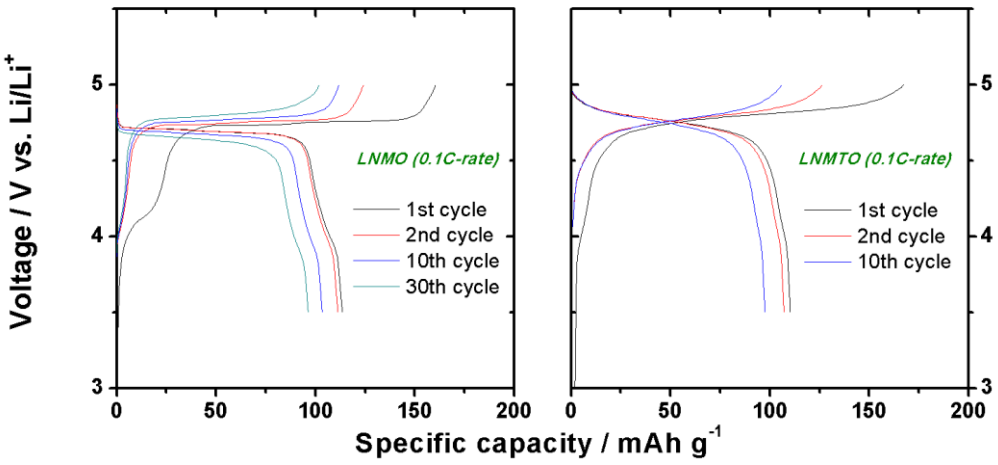

Figure 19: Charge and discharge curves of $LiNi_{0.5}Mn_1T_{i0.5}O4$ and $LiNi_{0.5}Mn_1Ti_{0.5}O_4$ synthesized by sol-gel method

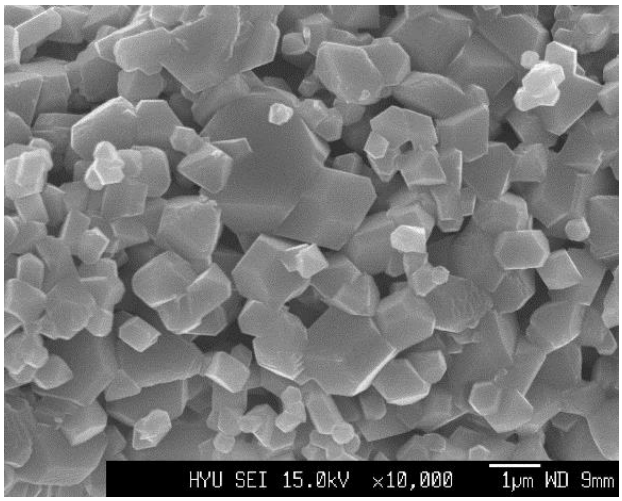

Figure 20: SEM image of $LiNi_{0.5}Mn_{1.0}Ti_{0.5}O_4$ synthesized by solid-state reaction method.

Figure 19 shows the electrochemical properties of $LiNi_{0.5}Mn_{1.5}O_4$ and $LiNi_{0.5}Mn_{1.0}Ti_{0.5}O_4$ synthesized by sol-gel method. The cell tests were carried out under 0.1 C-rate current in the voltage window from 3.5 to 5 V at room temperature. In the Figure, there is a plateau at around 4.7V, which indicates the $Ni^{2+/4+}$ redox during cycling. $LiNi_{0.5}Mn_{1.5}O_4$ sample delivers around 120 mAh/g of initial discharge capacity. For the $LiNi_{0.5}Mn_{1.0}Ti_{0.5}O_4$ cell, it shows 110 mAh/g of initial discharge capacity that is smaller than those of $LiNi_{0.5}Mn_{1.5}O_4$ cell. This is because Ti-substitution made electric conductivities lower, so the electrochemical performances slightly decreased. In earlier studies, $LiNi_{0.5}Mn_{1.0}Ti_{0.5}O_4$ synthesized by using solid-state reaction method had large micron-sized particles (Figure 20) and delivered only 100 mAh/g (Figure 3). In contrast, $LiNi_{0.5}Mn_{1.0}Ti_{0.5}O_4$ synthesized by using sol-gel methods in this study delivered larger initial capacity of 110 mAh/g. Although this specific capacity value is much lower than theoretical capacity (149.6 mAh/g), this capacity increase could be partly explained by the increase in reversible Li-ions in the spinel by decreasing Li-ion diffusion length (i.e., smaller particle sizes). The same approach (i.e., engineering nano-particles) has been taken to

utilize the full capacity of $LiFePO_4$. Therefore, it validates our hypothesis that the decreasing capacity from Ti-substitution in $LiNi_{0.5}Mn_{1.5-x}Ti_xO_4$ is attributed to the decreasing electronic conductivity with increasing Ti contents.

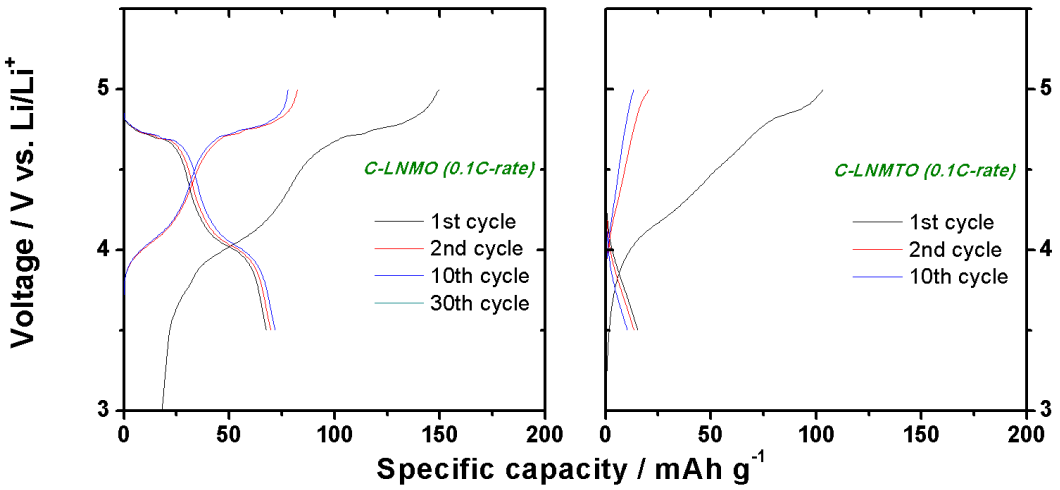

Figure 21: Charge and discharge curves of carbon-coated $LiNi_{0.5}Mn_{1.5}O_4$ and $LiNi_{0.5}Mn_1Ti_{0.5}O_4$ heated in Argon atmosphere

Figure 21 shows the cycling results of carbon-coated LNMO and LNMTO heated in Ar atmosphere. In terms of LNMO cathode, it shows approximately 70 mAh/g of discharge capacity at first cycle, which means the performances of cathode decreased through carbon-coating. In terms of LNMTO cathode, the initial discharge capacity indicates around 20 mAh/g. It is originated from decomposition reaction when heating in Argon. From XRD patterns (see Figure 15, we could know that spinel structure is decomposed in Argon atmosphere at high temperature and transform to NiO, MnO, and other impurity phases. This decomposition reaction attribute to deteriorate the cell performances as shown in Figure 21.

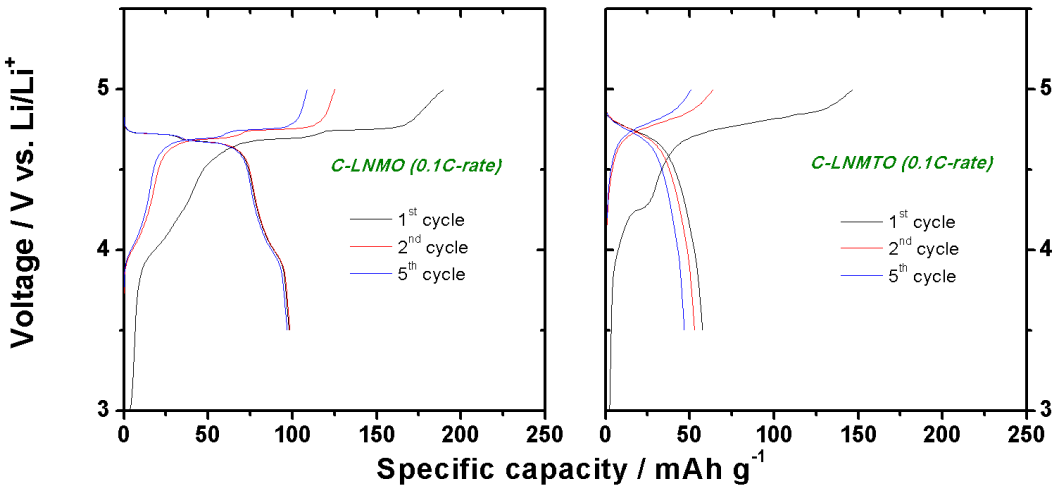

Figure 22: Charge and discharge curves of carbon-coated $LiNi_{0.5}Mn_1Ti_{0.5}O_4$ and $LiNi_{0.5}Mn_1Ti_{0.5}O_4$ heated in Argon atmosphere

Figure 22 shows the cycling result of carbon-coated LNMO and LNMTO heated in air atmosphere. For LNMO cathode, it shows a discharge capacity around 100 mAh/g at the first cycle, comparing to the capacity (shown in Figure 18) of synthesized LNMO using the sol-gel method, the capacity of the coin cell decreased. Same pattern also applied to the carbon-coated LNMTO cathode, which the discharging capacity decreased to around 65-70 mAh/g. Overall, even though the original structures of both cathode materials were maintained, the electrochemical performance was negatively-affected by the carbon-coating process.

3.5 Rietveld Refinement analysis

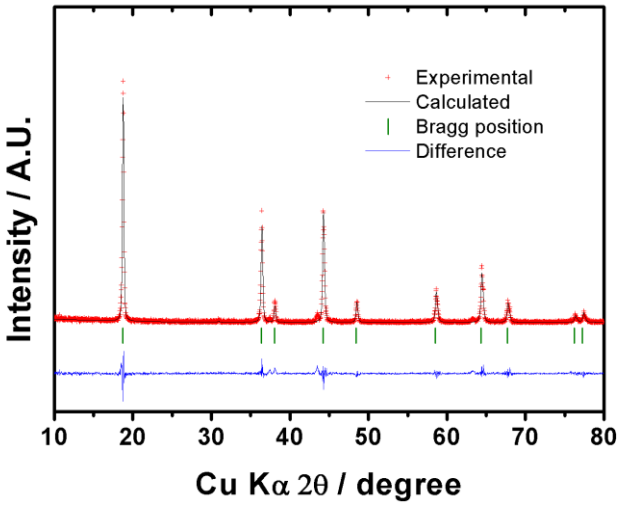

Figure 23: Rietveld refinement result of XRD patterns for LNMO. Red-cross marks means the records that observed by X-ray diffraction, black-line indicates the simulated patterns, olive-vertical marks indicate bragg peaks that shows in spinel structure, and blue-line means the differences between experimental and calculated values.

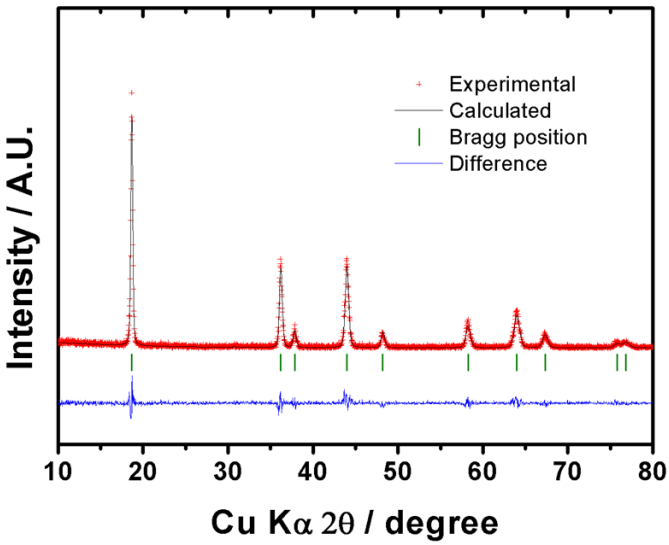

Figure 24: Rietveld Refinement result or XRD patterns for LNMTO.

Table 5: Rietveld refinement results of XRD data for LNMO and LNMTO

LNMO

Chem. form.		$LiNi_{0.5}Mn_{1.5}O_4$		
Crystal system		Cubic		
Space group		$Fd\bar{3}m$		
Atom	Site	x	y	z
Li	8a	0.125	0.125	0.125
Ni	16d	0.5	0.5	0.5
Mn	16d	0.5	0.5	0.5
O	32e	0.2605	0.2605	0.2605
Lattice parameter		a=b=c=8.16655 Å		
Unit cell vol.		544.648 $Å^3$		
R_{wp} (%)		27.889		

LNMTO

Chem. form.		$LiNi_{0.5}Mn_{1.0}Ti_{0.5}O_4$		
Crystal system		Cubic		
Space group		$Fd\bar{3}m$		
Atom	Site	x	y	z
Li	8a	0.125	0.125	0.125
Ni	16d	0.5	0.5	0.5
Mn	16d	0.5	0.5	0.5
Ti	16d	0.5	0.5	0.5
O	32e	0.2614	0.2614	0.2614
Lattice parameter		a=b=c=8.21968 Å		
Unit cell vol.		555.348 $Å^3$		
R_{wp} (%)		27.48		

The structural analysis is performed by using Rietveld refinement method in order to know the effect of Ti-substitution. From Figure 23 and 24, the experimental marks and calculated line are well-matched, which means our calculation is conducted well without error. According to Table 5, the structures of LNMO and LNMTO are basically same. Those have same spinel structure and space group, $Fd\bar{3}m$, but lattice parameters are slightly different each other. lattice parameters LNMO and LNMTO indicate 8.16655 and 8.21968 Å, respectively. Since it has cubic structure (lattice parameter a=b=c and $\alpha=\beta=\gamma=90^o$), the unit cell volume of LNMTO is significantly bigger than LNMO. Ti-substitution makes volume of the unit cell enlarge, which allows that lithium ion can transfer faster through the expanded lithium channels in the structure as shown in Figure 25.

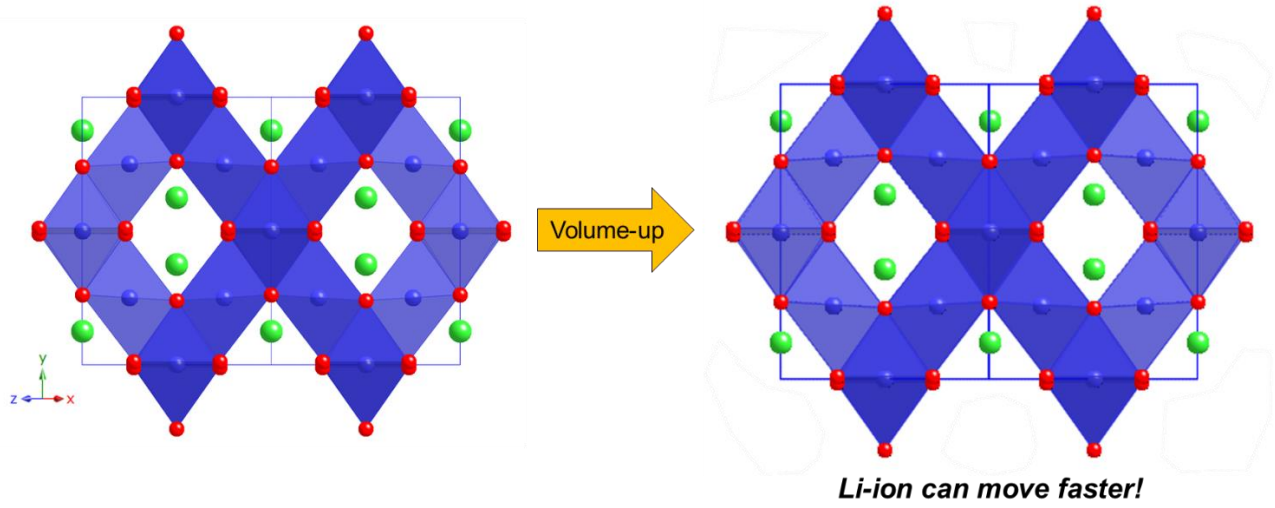

Figure 25: Schematic images of the effect of Ti-substitution in spinel system. Expanded volume of the unit cell allows lithium ion migration faster.

Chapter 4 Conclusion

4.1 Contribution

Lithium battery is one of the most popular power source in current industry. It's wide range of application affect people's daily life and cathode material is the one of the most crucial component that limit the development of lithium-ion battery since it determined the capacity of the battery. As a promising cathode material, $LiNi_{0.5}Mn_{1.5}O_4$, with the advantage of high capacity and low cost, the barrier from put this material into implementation of application, especially for electric vehicle, its short cycle life, and its improvements material, $LiNi_{0.5}Mn_1Ti_{0.5}O_4$ has to sacrifice the advantage of capacity to improve its cycle life. Through this research, by understanding the fundamental principle of the capacity fading for

$LiNi_{0.5}Mn_1Ti_{0.5}O_4$, we can find the right way to improve its electrochemical performance, and made this material available to put into actual production.

4.2 Future Work

If given more time, I would repeat the test for a few more times with different compositions of material to gain a comprehensive data. I would synthesize $LiNi_{0.5}Mn_{1.45}Ti_{0.05}O_4$ to $LiNi_{0.5}Mn_{0.5}Ti_1O_4$ to confirm the effect of Ti substitution for Mn and its effect on the capacity of battery. For material synthesis, I would tried synthesize LNMO and LNMTO in different temperature for heat treatment (e.g. 900℃) to see its impact on crystallinity of the material.

In addition, instead of hand grinding, I would utilize high energy ball milling machine to decrease the particle size. Using this machine would let the particle size for the material to be more uniform while without affecting its original crystallinity.

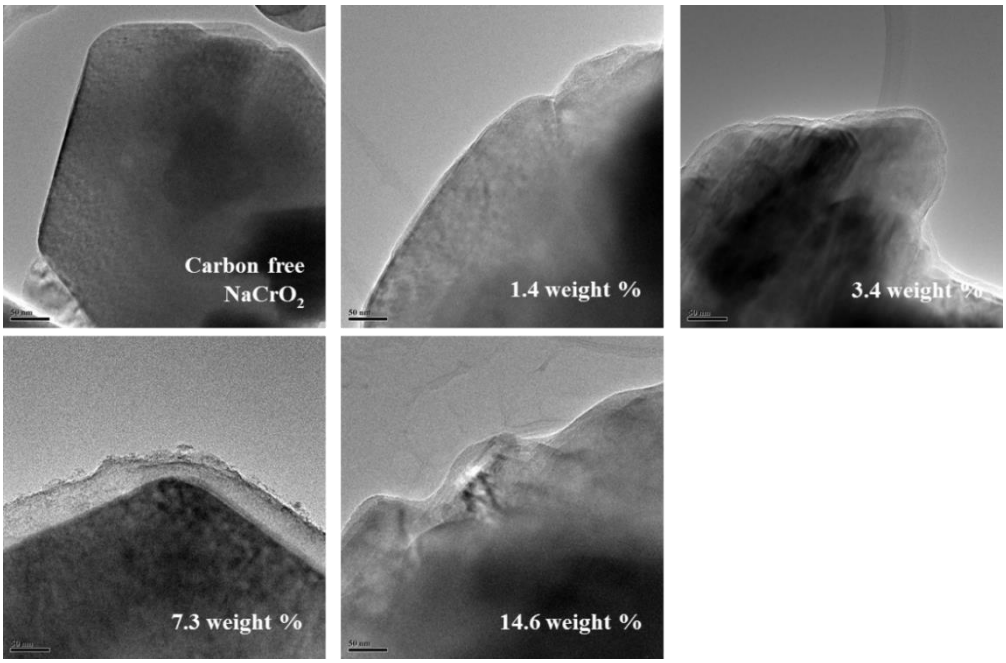

Figure 26: *TEM images of bare and carbon-coated $NaCrO_2$.*

I would also try different technique for carbon coating to see the effect of different approach. For example, I would conduct high-energy ball milling of LNMTO with different types of carbons such as graphene or acetylene black shown in Figure 26[8]. The second approach is to apply metallic conductive coating by using plasma sputtering method. In addition, I would also see the weight percent of conductive coating and its affection on the batteries capability. I would verify coated layers on particle surfaces using energy-dispersive X-ray spectroscopy (EDS) attached at SEM and transmission electron microscopy (TEM).

At last, I would tried coin cell test at different charging rate and observed the cycle life of the batteries. Cycle life is also an important data for battery and I would like to examine if different types or weight percent of carbon coating would impact the cycle life of the battery.

4.3 Summary

In conclusion, LNMO and LNMTO were successfully synthesized using sol-gel method and the primary particle size was decreased to Nano-scale comparing to the traditional solid-state method. The secondary particle size was also decreased by hand grinding. Errors were found in the carbon coating process, while decomposition reaction were observed in Argon atmosphere, by changing the carbon coating method, conductive coating were successfully applied to LNMO and LNMTO in air atmosphere. Through the coin cell test result, the specific capacity were improved which verified Dr. Kim's assumption that Ti content in $LiNi_{0.5}Mn_{1.5-x}Ti_xO_4$ reduce the charge carrier (i.e., electron) concentration. By understanding this principle, LNMTO could reached the desired capacity and may be put into production for future electric vehicle.

Reference

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